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Design of SRU thermal reactor and waste heat boiler considering recombination reactions

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Abstract

The first section of sulphur recovery units (SRU) based on Claus process is constituted of a burner, a thermal reactor and a waste heat boiler and it is designed to oxidize acid gases by air. Because of several oxidation reactions are reversible, as the gas is cooled in the boiler recombination reactions occur, modifying the heat exchange and gas composition. This may have a significant effect on the design of the waste heat boiler and downstream Claus reactors. In this study, the design of thermal reactor and waste heat boiler system is proposed by adopting a common model. The model, including a detailed kinetic scheme, considers recombination reactions in the boiler.

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Keywords: Sulphur recovery unit; waste heat boiler; kinetics.

1. Introduction

The Claus process is the most common route for recovering sulphur from acid gases coming from oil and gas desulphurization treatment. Typically, a SRU is composed of a burner, a thermal reactor (TR), a waste heat boiler (WHB) (Fig. 1) and a train of sulphur condensers and catalytic Claus reactors. The acid gas, which is mainly constituted of H₂S, H₂O, CO₂, CO, NH₃ and hydrocarbons, is mixed with air and

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oxidized at high temperature by means of the burner and TR, which provides for the necessary residence time. Next, the gas is cooled down in the WHB and the first condenser, and sent to the first Claus reactor.

Nomenclature

C	Species concentration ($\text{mol}\cdot\text{m}^{-3}$)
C_p	Specific heat at constant pressure ($\text{J}\cdot\text{kg}^{-1}\cdot\text{°C}^{-1}$)
D	Diameter (m)
ΔH	Heat of reaction ($\text{J}\cdot\text{mol}^{-1}$)
E	Activation energy ($\text{J}\cdot\text{mol}^{-1}$)
h	Heat transfer coeff. ($\text{W}\cdot\text{m}^{-2}\cdot\text{°C}^{-1}$)
k	Kinetic constant ($\dots\cdot\text{s}^{-1}$)
K	Rate of reaction ($\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$)
M	Molecular weight ($\text{kg}\cdot\text{kmol}^{-1}$)
P	Pressure (kPa)
R	Universal constant of gas ($\text{J}\cdot\text{mol}^{-1}\cdot\text{°C}^{-1}$)
T	Temperature (°C or K)
v	Velocity ($\text{m}\cdot\text{s}^{-1}$)
x	Axial coordinate (m)
m	Mass fraction (-)
y	Molar fraction (-)
μ	Dynamic viscosity ($\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-1}$)
λ	Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{°C}^{-1}$)
ρ	Density ($\text{kg}\cdot\text{m}^{-3}$)

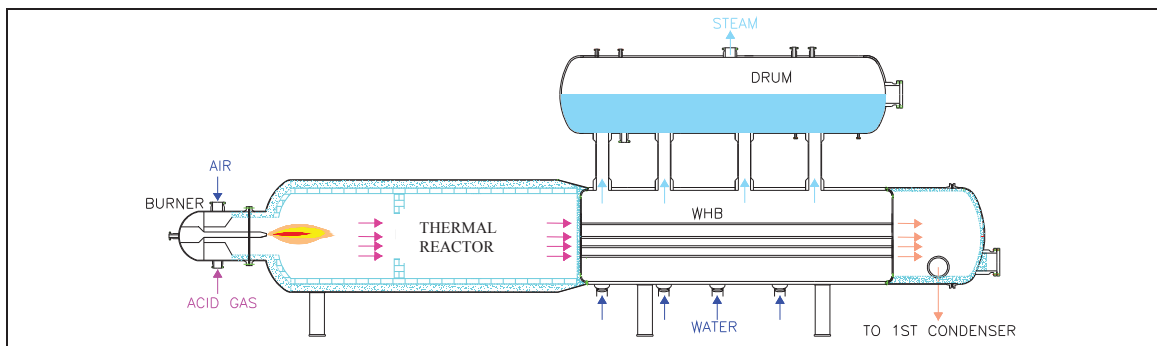


Fig. 1. Layout of a typical SRU WHB package.

The key oxidation reaction occurring in the TR is:



where a third of the H_2S is consumed by proper stoichiometric amount of oxygen; other oxidation reactions lead to formation of elemental sulphur (S or S_2). Also thermal decomposition of H_2S in the TR is an important recovering reaction, which gives significant amount of H_2 and sulphur. The residual H_2S is

oxidized in the downstream Claus reactors by the SO_2 produced in TR and alumina-based catalyst according to the overall reaction:



which elemental sulphur is next removed by condensation.

The TR is an axial-symmetric chamber internally lined by refractory in order to prevent overheating on vessel walls. The WHB is used for cooling the hot gas leaving the TR to an operating temperature suitable for next sulphur condensation and catalytic oxidation. This boiler, directly connected to the TR, is of shell-and-tube type, with gas flowing on tube-side in one or two passes, and with boiling water on shell-side. Either a kettle type boiler or a boiler-and-drum package is used; a moderate slope towards outlet of tubes may be installed for draining possible liquid sulphur. Boiling water performs a rapid and effective removal of heat. Depending on acid gas composition, temperature of combusted gases in the TR is in a range of 1100 to 1400°C; at the boiler outlet, temperature is around 300°C. However, the cooling is not so rapid to prevent recombination reactions, which one of the most important is:



Also CO can recombine with S_2 to form mercaptans. Recombination reactions are viable until relevant quench temperatures are reached and gas composition is frozen; typically, below 900-1000°C recombination is quenched. As a consequence, exchanging tubes of the boiler work as non-adiabatic plug flow reactors.

Taking into account recombination reactions in the design of the WHB is important. Such reactions are mainly exothermic; therefore, they give an additional release of heat. This may have an impact on boiler heat transfer surface, number and operating temperature of tubes. From a process plant standpoint, recombination downgrades the gas composition as hydrogen sulphide and mercaptans are formed: the performance of the sulphur recovery is lowered and the required amount of SO_2 in reaction (r.2) is increased, along with the amount of oxidation air, blower power consumption and equipment volumes.

A model for the design of the TR and WHB is described hereby. Following a previous work investigating quench times in a waste heat boiler [1], the computational model is written for a mono-dimensional geometry and stationary conditions, and it is constituted of energy and chemical species conservation equations. Oxidation and recombination reactions are taken into account considering a detailed kinetic scheme [2]. The study shows that TR and WHB can be considered a single unit, which design is done by a common computational model.

2. Description of the model

Oxidation of acid gas starts in the burner flame and continues along the TR until a thermodynamic equilibrium is reached. Due to high temperature and residence time (usually >1.0s), gas composition entering the WHB is about at equilibrium. As the gas is cooled in the WHB, equilibrium and kinetics are shifted. Considering a typical WHB of fire-tube, one-pass type, directly connected to the TR, the gas is evenly distributed in the horizontal tubes, whereas on shell-side water is in boiling conditions. As tubes are identical and immersed in a pool, they are independent one other; as a consequence, one tube only is representative of the WHB. Operating pressure and pressure drop are in the range of 150 kPa(a) and 3 kPa; therefore, the momentum equation can be dropped without significant effect on thermal-fluid-dynamics parameters. As the gas is characterized by high Reynolds and Peclet numbers, diffusive terms can be neglected. The flow is assumed to be fully developed both in TR and WHB, with flat profiles across the sections. This assumption can be considered acceptable even in case of swirling flow in the TR provided that residence time is large and resulting fluid-dynamics is axial-symmetric like. Accordingly,

the TR and the WHB work as a plug flow reactor; resulting energy and species conservation equations are:

$$\frac{d}{dx}(\rho v C_p T) = h \frac{4}{D} (T - T_{ext}) - \sum_r (\Delta H_r) K_r \quad (1)$$

$$\frac{d}{dx}(v C_i) = \sum_r K_{r,i} \quad (2)$$

with the reaction rate, K , of generic form:

$$K_{r,i} = k_{r,i} C_i^\alpha C_j^\beta e^{-E_r/RT} \quad (3)$$

where subscripts ext , r and i,j refer to external fluid, chemical reactions and species, respectively. Eq. (1) and (2) describe temperature and gas composition along both TR and WHB tube axis. The first right-hand-side term of Eq. (1), which represents the heat exchanged with ambient, air for TR and water for WHB, allows differentiating the equipment. For TR, the heat transfer is negligible as a considerable refractory layer is installed; therefore, the overall heat exchange coefficient, h , is small and the TR works practically as an adiabatic plug flow reactor. On the contrary, the coefficient h is large for the WHB, and the tube works as a non-adiabatic plug flow reactor. As a result, Eq. (1) and (2) can be adopted for the design of the TR-WHB system provided that h , D and T_{ext} are changed as the coordinate x corresponds to the inlet of tubes.

Due to operating conditions, an ideal scheme is assumed for density of the gas; specific heat is obtained by a weighted average of heats of species i . Chemical-physical quantities, viscosity and thermal conductivity, are obtained by correlations based on composition and temperature, as Chapman-Enskog-Wilke and Wassiljewa-Mason-Saxena schemes (Eq. 6 and 7), respectively:

$$\rho = \frac{P}{RT} \sum_i y_i M_i \quad (4)$$

$$C = \sum_i m_i C_i (P_{inlet}, T) \quad (5)$$

$$\mu = \sum_i \frac{y_i \mu_i (P_{inlet}, T)}{\sum_j y_j \Phi_{i,j}} \quad (6)$$

$$\lambda = \sum_i \frac{y_i \lambda_i (P_{inlet}, T)}{\sum_j y_j \Psi_{i,j}} \quad (7)$$

As a case study, hereby fouling is not considered for WHB tubes (clean conditions); under this assumption, the overall heat transfer coefficient is determined, with good approximation, only by gas as boiling water and tube wall present a heat transfer resistance of two orders of magnitude greater than the resistance of gas flowing in tubes. The coefficient h is obtained by a typical turbulent flow correlation, including Reynolds and Prandtl numbers:

$$h = \frac{\lambda}{D} 0.023 \left(\frac{\rho v D}{\mu} \right)^{0.8} \left(\frac{\mu C_p}{\lambda} \right)^{0.33} \quad (8)$$

Kinetics of acid gas combustion and recombination is quite complex, involving several tens of species, including radicals, and it has not been clearly and comprehensively defined yet. Reviews of thermodynamics and kinetics have been given in literature [3,4,5]. For this study, an overall kinetic scheme involving no. 130 species and more than 1500 reactions has been implemented [2].

Eq. (1) to (8) form a differential-algebraic stiff system. Computational stiffness arises for the presence of radical species in the kinetics scheme. Solution is obtained by Gear multi-value method with variable order and integration step, based on Newton method. Such methods are implemented in the BzzMath® library [6], an OOP and parallelized (openMP) computing package.

3. Results

The described model has been applied to two operating systems. For the first, inlet acid gas and combustion air compositions are given, and the TR-WHB system is modelled as a single plug flow reactor. For the second system, the model is applied to the WHB only, for a given combusted gas composition at the inlet of tubes. Inlet operating conditions and geometrical parameters are reported in Tables 1 and 2; computational results are reported in Fig. 2 and 3.

For system 1, results show that the gas temperature is at uniform temperature in the TR and composition is about at equilibrium at the inlet of tubes. At $x=6.5\text{m}$, the overall heat transfer coefficient h has a steep increase, and thermodynamics and kinetics are suddenly shifted by the cooling of gas. Recombination occurs and significant amount of H_2S is formed. SO_2 and CO_2 are formed and consumed respectively; as there is no free oxygen, the SO_2 acts as an oxygen pusher. Also COS is formed. Recombination is quenched at $x=7.5\text{m}$ approx., which corresponds to a residence time in the WHB tube of 0.25s and to a gas temperature of 900°C about; then, gas composition is frozen till outlet of tubes. This is in line with experimental observations and results discussed in previous literature [1,7].

Same considerations for Fig. 3, except for the very first portion of tubes where H_2S is temporarily formed. This is due to the fact that the inlet combusted gas composition in Table 2 is not at equilibrium; then, hydrogen and elemental sulphur are recombined into hydrogen sulphide. After 2m from the tube inlet, the recombination is quenched.

4. Conclusions

Thermal reactors and waste heat boilers operating in sulphur recovery units can be considered a single plug flow reactor. The thermal reactor represents the adiabatic portion, whereas the boiler the non-adiabatic one. Accordingly, as proposed in the paper, they can be designed by the same model, provided that the heat transfer is properly set along the axial coordinate. The model takes into account the recombination reactions arising along the boiler tube. This recombination is responsible for an additional release of heat and a significant change in gas composition. As shown by results, the gas is about

thermally and chemically at equilibrium in the thermal reactor by installing a proper residence time; recombination appears, mainly for H₂S, in the first part of boiler tubes; as the gas is cooled down to a quench temperature, 900°C approx., recombination is ceased and composition is frozen.

Table 1. Inlet operating conditions and geometry parameters (system 1).

Acid gas composition (% vol)	H ₂ S=0.7955, CH ₄ =0.021, C ₂ H ₆ =0.0140, C ₃ H ₈ =0.0198, BUT12=0.0011, H ₂ O=0.0640, CO=0.0032, CO ₂ =0.0662, H ₂ =0.0037, NH ₃ =0.0048
Acid gas flow rate (kg/h)	4230.5
Acid gas temperature (°C)	125.0
Combustion air composition (% vol)	H ₂ O=0.0970, N ₂ =0.7138, O ₂ =0.1892
Combustion air flow rate (kg/h)	8907.1
Combustion air temperature (°C)	45.0
Operating pressure in TR (kPa(a))	159.0
TR internal diameter (m)	1.550
TR length (m)	6.500
Heat losses for TR (constant) (kW/m ²)	3.500
Boiling water temperature in WHB (°C)	204.0
WHB tube number (-)	470
WHB tube internal diameter (m)	0.050
WHB tube length (m)	6.000

Table 2. Inlet operating conditions and geometry parameters (system 2).

Gas composition at WHB inlet (% vol)	S _x =9.200, COS=0.028, H ₂ S=6.023, SO ₂ =3.025 H ₂ O=25.664, CO=0.019, CO ₂ =0.604, N ₂ =53.539, H ₂ =1.899
Gas flow rate (per tube) (kg/h)	129.932
Gas temperature at WHB inlet (°C)	1351.0
Gas pressure at WHB inlet (kPa(a))	162.6
Boiling water temperature in WHB (°C)	201.2
WHB tube internal diameter (m)	0.048
WHB tube length (m)	9.150

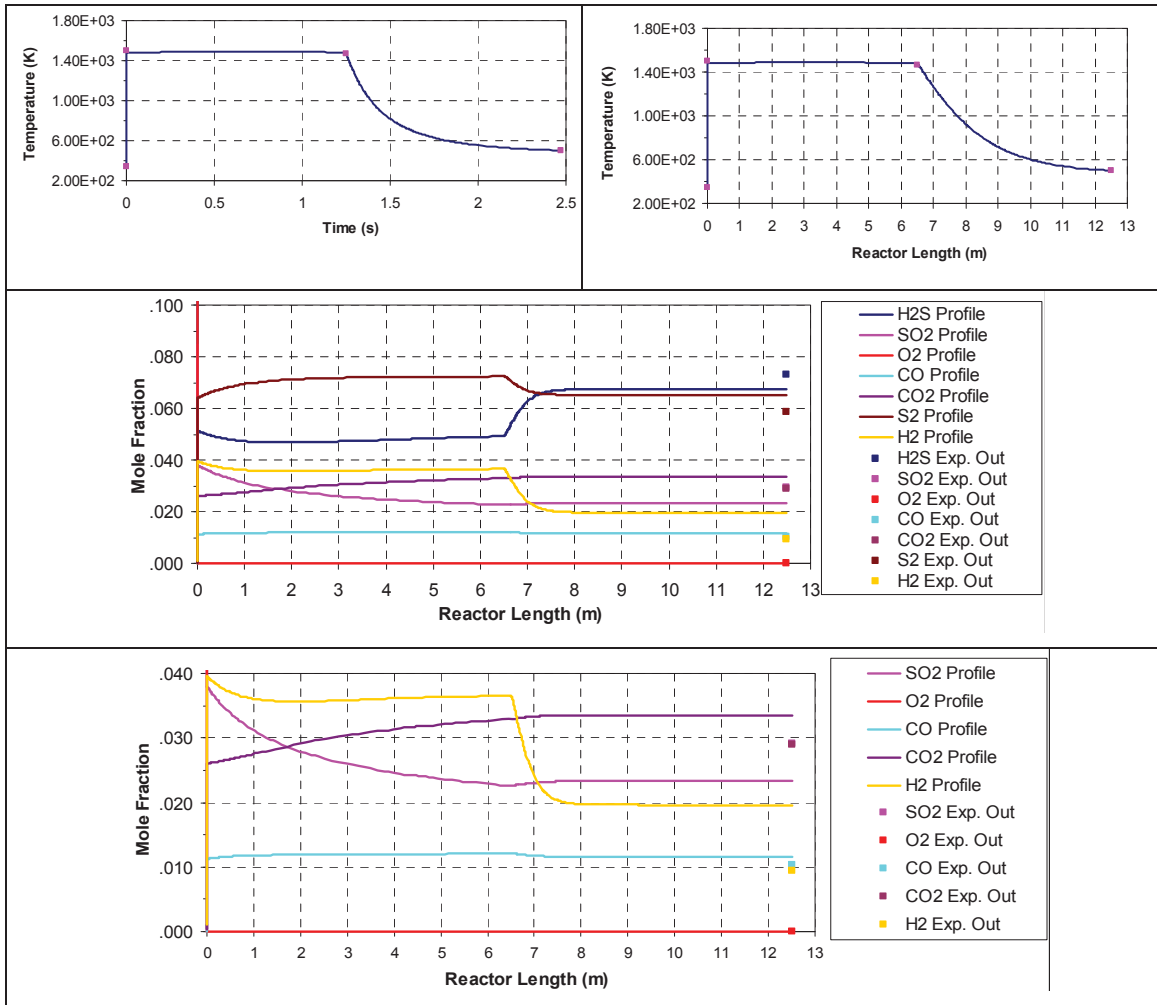


Fig. 2. System 1 - Gas temperature versus residence time (left-top) and axial coordinate (right-top), and gas composition profiles.

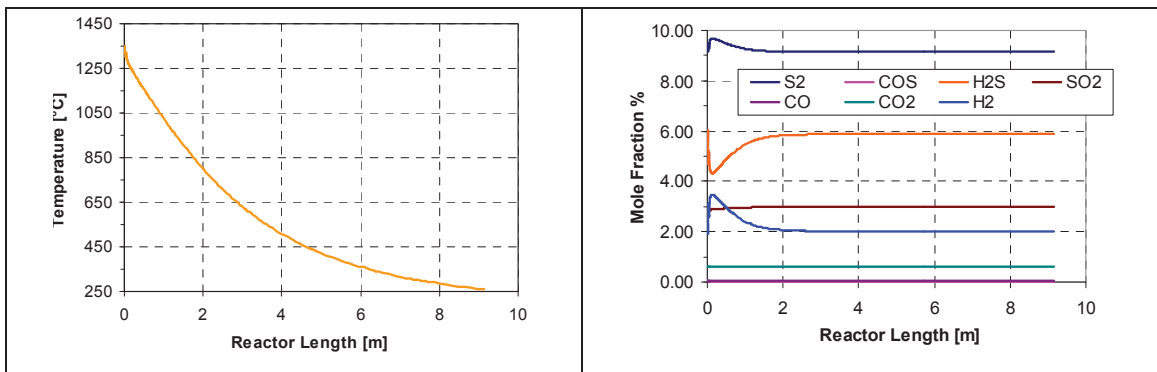


Fig. 3. System 2 - Gas temperature (left) and gas composition (right).

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